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Thermodynamic and Chemical Parameters of the Exhaust Effluents From the HARPOON Booster Motor

J. Briscoe Stephens and Arnold I. Goldford

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FOREWORD

A part of the general philosophy associated with the investigation reported herein was the transfer of the NASA plume chemistry technology to the U.S. Navy to establish an in-house capability in the Navy so that any required subsequent analysis of similar rocket motors can be performed. The procedures, computer programs, users' manuals, and input are at the Naval Surface Weapons Laboratory, Dahlgren, Virginia.

This study was accomplished in response to a request from the Naval Surface Weapons Laboratory as given in Navy Work Order Number N60921-76-MP-RD083. This report has been reviewed by J. W. Hill of the Naval Surface Weapons Laboratory and approved for publication. It contains no classified information.

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THERMODYNAMIC AND CHEMICAL PARAMETERS OF THE EXHAUST EFFLUENTS FROM THE HARPOON BOOSTER MOTOR

I. INTRODUCTION

Analytical techniques were utilized to predict the thermodynamic and thermochemical interactions of the HARPOON rocket exhaust plume with the ambient atmosphere to ascertain the resulting chemical species and their respective concentrations so that the localized influence on the air quality could be assessed.

When a solid propellant missile such as the HARPOON is launched, the hot exhaust effluents form a cloud behind the vehicle. The plume and the ambient atmosphere interact in a complex manner that is dependent in part on vehicle parameters such as chamber pressure, propellant ingredients, trajectory, and the prevailing ambient atmospheric conditions [1]. Without analytical predictions, it could be postulated that the elements in the propellant ingredients and the air form a voluminous number of chemical species — some of which are highly toxic even in small concentrations. Thus, an analytical prediction of the thermodynamic and thermochemical interactions that occur in the exhaust plume is utilized to eliminate those species that cannot be formed. The analytical prediction is obtained utilizing the following analyses techniques:

a. Thermodynamic Analysis (Step 1) — This analytical technique is used to examine the exhaust constituents to determine if temperatures and pressures are conducive to promote the formation of various species.

b. Finite-Rate Chemical Analysis (Step 2) — Using the candidate species selected and their postulated chemical reactions, this analysis technique examines the kinetics of the flow field to determine if the residence time of the constituents is long enough for the postulated reaction to occur. Thus, the analytical predictions provide the species present and their concentrations.

The results are applicable only for the rocket motor under investigation since changes in propellant ingredients, chamber temperature and pressure, or in the internal flow field will result in different exhaust products.

The analytical techniques discussed in this report serve two purposes. First, the exhaust species that are present and their concentrations in the plume are identified. If all the identified species are nontoxic, then no further action is required. However, if potentially toxic species do exist, it may be desirable to monitor the exhaust effluents. A secondary purpose of the analysis is to identify species that are easily monitored and determine their constancy in relationship to other species that are of primary interest. A hypothetical example is that both sulfur and chlorine compounds are present and the sulfur compound is easily and accurately measured, whereas the chlorine compound is difficult to measure. If the analysis indicates that the ratio of the sulfur compound concentration to the chlorine compound concentration is fairly constant, it is sufficient to measure only the sulfur compound concentration. The use of the naturally occurring tracer will allow accurate measurements to be made easily and inexpensively.

The analytical techniques discussed in this report are applicable not only to the HARPOON booster but to any solid propellant rocket-powered missile. In addition, the computer codes, the necessary users' manuals, and the input and output of all of the computer runs generated during this investigation have been delivered to the appropriate personnel at the Naval Surface Weapons Center, Dahlgren, Virginia.

A general discussion of the overall analysis scheme that was utilized in the investigation is given in Section II. Section III is a discussion of the thermochemical analysis and the error in the thermodynamic data utilized in portions of the analysis. Section IV is a discussion of the nozzle analysis and afterburning analysis performed. Section V gives the results, conclusions, and recommendations.

II. GENERAL TECHNICAL APPROACH

The general approach used in this study was as follows. First, a one-dimensional thermochemical analysis of the propellant was performed. Second, utilizing these results for the species, pressures, one-dimensional combustion product velocities, etc., a more realistic two-dimensional, two-phase analysis of the HARPOON motor nozzle was performed for the exit plane value of species, temperatures, pressures, and velocity. Finally, utilizing the results from the two-dimensional analysis, the one-dimensional thermochemical analysis was redone to obtain a realistic estimate of the species present at the motor nozzle exit and their concentration. Simultaneously, a study was performed to determine

the accuracy of the thermodynamic data utilized in the study, which is primarily obtained from spectroscopic constants. An estimate was made of the effect of the thermodynamic data accuracy on the species concentration. Using an available two-dimensional, finite-rate chemical mixing analysis, the plume emanating from the HARPOON motor nozzle was analyzed to obtain the species and their concentration and the local static temperature as a function of axial and radial distance from the nozzle exit. For some of the trace chemical species for which there were no data available on possible finite-rate reactions, the concentration of the trace species was obtained by assuming an infinite rate for the reaction, i.e., an equilibrium calculation was made which yielded the largest possible concentration that could be present.

III. THERMOCHEMICAL ANALYSIS FOR EXIT PLANE SPECIES AND CONCENTRATIONS

A. Background

The initial step in determining the HARPOON booster exhaust products that are to be employed in the air quality assessment is to eliminate as many candidate species as possible by a thermochemical analysis assuming chemical equilibrium. Basically, in this analysis the chamber and nozzle temperatures and pressures are used to determine the chemical reactions which can occur without considering reaction times, hence obtaining the maximum number of species and their concentrations that can be present in the exhaust effluents. To explain in greater detail, a summary discussion of the One-Dimensional Equilibrium (ODE) code will be given in terms of how it functions and its data requirements. In this section, specific attention will be given to the effect of the dynamics of the rocket on the species concentration and the treatment of competing reactions. The reliability of the spectroscopic data used in ODE will also be discussed.

To determine what species will be present and in what concentration, a computer simulation of rocket firings was conducted with the one-dimensional thermochemical nozzle analysis program (ODE). The input for the analysis consists of the solid propellant composition and heat of formation, the HARPOON motor geometric specifications, and the chamber pressure history. The ODE computer program [2] determines the chemical species and their concentration at chemical equilibrium for a given motor condition, i.e., chamber pressure and area ratio. The resulting species of the equilibrium calculations were used

as input to the nozzle analysis and afterburning calculations. Inherent in the calculation of the chemical species and their concentration are the potential errors in the thermodynamic data which produce some uncertainty in the concentration of chemical species.

The chemical species present in the combustion chamber and their concentrations depend on the combustion temperature. The combustion temperature depends on the enthalpy of the propellant ingredients and the chemical species formed in the combustion process. The solution of such a cyclic interaction is calculated by a one-dimensional thermochemical program. One of the required inputs to such a program is the propellant ingredients and their enthalpy. The HARPOON booster propellant formulation and enthalpy used is given in Table 1. It should be noted that the propellant contains 78.5 percent of a highly reactive compound, ammonium perchlorate, as an oxidizer.[1] The use of such an oxidizer implies that the combustion products should contain significant quantities of chlorine species. A motor parameter which is significant when calculating the exhaust species is the expansion or area ratio of the nozzle. Table 2 [3] gives some of the important geometric parameters of the HARPOON booster. An additional discussion of the significance of some of the parameters as they apply to the finite-rate analysis is given in Section IV.

TABLE 1. HARPOON PROPELLANT COMPOSITION

Ingredient	Weight Percent
Ammonium Perchlorate	78.5
Aluminum	6.0
Copper Chromite	2.0
Sulfur (Flowers)	0.1
Binder (PU)	13.4
Enthalpy of propellant (cal/mode)	-27830.

The chemical species computed in the one-dimensional equilibrium thermochemistry program are based on the chemical composition of the propellant and the chemical compounds in the program data base. First, all species that are chemically possible for the propellant under consideration are identified. Based on thermochemical data, the compounds listed in Table 3 [4]

1. Private communication from Dr. Glen Moore, Naval Surface Weapons Center, July 1975.

TABLE 2. HARPOON MOTOR PARAMETERS

Throat Diameter	2.23 in.
Throat Area	3.91 $in.^2$
Nozzle Diameter	6.40 in.
Nozzle Area	32.17 $in.^2$
Nozzle/Area Ratio	8.24

TABLE 3. CHEMICAL SPECIES CONSIDERED

Cu	NH	H	COS	Al_2O_2
Al	S	HCO	C_2Cl_2	C
$AlCl_3(L)$	SO_2	H_2O	C_2O	CH
AlO	$Cr_3C_2(S)$	NO	ClO	CH_4
AlO_2H	CuCl(L)	N_2	CR(S)	CO
$Al_2O_3(S)$	Cu(L)	O	HALO	CO_2
CCl	AlCl	SH	HNO_2	C_2H
CH_2	$AlCl_3$	SO_3	H_2O_2	C_3O_2
CN	AlOCl	$Cr_7C_3(S)$	NOCl	ClO_2
COCl	Al_2Cl_6	CuCl	N_2O	CR(L)
CS	$Al_2O_3(L)$	CuO	OH	HCl
C_2N	CCl_2	$AlCl_2$	SN	HO_2
Cl	CH_2O	AlN(S)	SO_2Cl_2	H_2S
Cl_2	CNN	AlOH	$CrCl_2(S)$	NO_2
Cr	$COCl_2$	Al_2O	CuH	NH_2
HCN	CS_2	C(S)	Cu_2	O_2
H_2	C_2N_2	CCl_3	$AlCl_3(S)$	SO
NH_3	ClCN	CH_3	AlN	S_2
NO_2Cl	Cl_2O	CN_2	AlO_2	$Cr_2O_3(S)$

were selected as the basic candidate set of species. The analyzer then determined which of the various chemical species existed in the simulated HARPOON motor. The thermochemical data required for this analysis included the heat capacity (C_p), entropy (S), enthalpy (H), Gibbs free energy (G), and equilibrium constants (K_p) as a function of temperature. Finally, these data were used by the thermochemistry program to compute the concentrations of the chemical species in the chamber, throat, and exit plane based on the propellant enthalpy and the temperature and pressure that occurred locally.

As previously noted, the concentration of a species is a function of the chamber pressure and temperature. To demonstrate this, the first 2 sec of data for three trajectories of the HARPOON booster for each of three HARPOON launcher configurations, the Canister, Tarter, and ASROC, are tabulated in Table 4 [5]. The three different launcher configurations provide different angles of launch and initial launch positions relative to the ship's deck. This gives different angles of the missile centerline and ranges relative to the deck as a function of time. A chamber pressure history [6] is also provided in this table. Both sets of data were analyzed as a function of time. The analysis yielded range, velocity, and chamber pressure tabulations as a function of time (Table 4). Figure 1 shows the missile trajectory for the Canister launcher.

A series of computer runs was made to determine the concentration of chemical species at different time periods in the initial portion of the flight of the missile. The data for several pressures are given in Table 5. The species concentrations are at the 1-D exit plane. The 1800 psia is indicative of the chamber pressure just after the first motion out of the launcher. Table 5 lists only those compounds which contain significant concentrations (above 10^{-6} ppm). It can be seen that most species concentrations changed very little from the pressure at the initial phase to peak chamber pressures. Ammonia (NH_3), carbonyl chloride (COCl), and hydrogen cyanide (HNC) increased approximately 20 percent in concentration as the pressure increased to the peak. This is a small change over the 300 psia pressure differential. It is understandable because the equilibrium constant, K_p, for formation of products is very temperature dependent. Consequently, it is not critical that one investigate the impact of various chamber pressures, but it is more important to examine the portions of the plume where the temperature increases significantly.

In a combustion process, normally there are competing reactions between some of the species. The production of particular chemical species and their concentration under equilibrium combustion conditions at a given temperature

TABLE 4. RANGE, VELOCITY, AND PRESSURE VERSUS TIME SINCE MISSILE FIRST MOTION OUT OF LAUNCHER

Time (sec)	Chamber Pressure (psia)	Range from Deck (ft)			Velocity (ft/sec)		
		Tartar	ASROC	Canister	Tartar	ASROC	Canister
0.1	1800	10.8	19.7	17.9	44.9	108.6	115.27
0.2	1870	15.4	30.8	30.3	71.4	144.0	149.7
0.3	1875	23.1	45.9	46.3	99.8	177.0	180.9
0.4	1930	34.0	64.8	65.8	128.5	211.3	214.1
0.5	2080	48.2	87.3	88.6	162.8	246.2	246.6
0.6	2100	65.8	113.4	114.7	186.5	280.3	278.3
0.7	2110	85.7	142.9	143.9	226.4	314.1	309.5
0.8	2100	110.1	175.8	176.3	265.8	347.6	340.6
0.9	2000	138.2	212.1	211.8	288.1	379.4	371.6
1.0	1960	168.7	251.5	250.4	322.4	412.6	402.5
1.1	1955	202.4	294.4	292.1	352.7	445.6	433.0
1.2	1950	239.2	340.5	336.8	384.2	477.7	463.0
1.3	1950	279.2	389.8	384.5	414.9	510.0	492.7
1.4	1950	322.2	442.4	435.1	445.1	541.4	521.7
1.5	1950	368.3	497.9	488.6	475.5	570.7	550.2
1.6	1945	417.2	556.5	544.9	505.2	602.1	578.1
1.7	1945	469.2	618.1	604.0	534.9	630.8	605.2
1.8	1940	524.1	682.5	665.8	562.7	658.7	631.4
1.9	1910	581.6	749.7	730.1	589.8	686.0	656.3
2.0	1890	642.1	819.5	796.9			

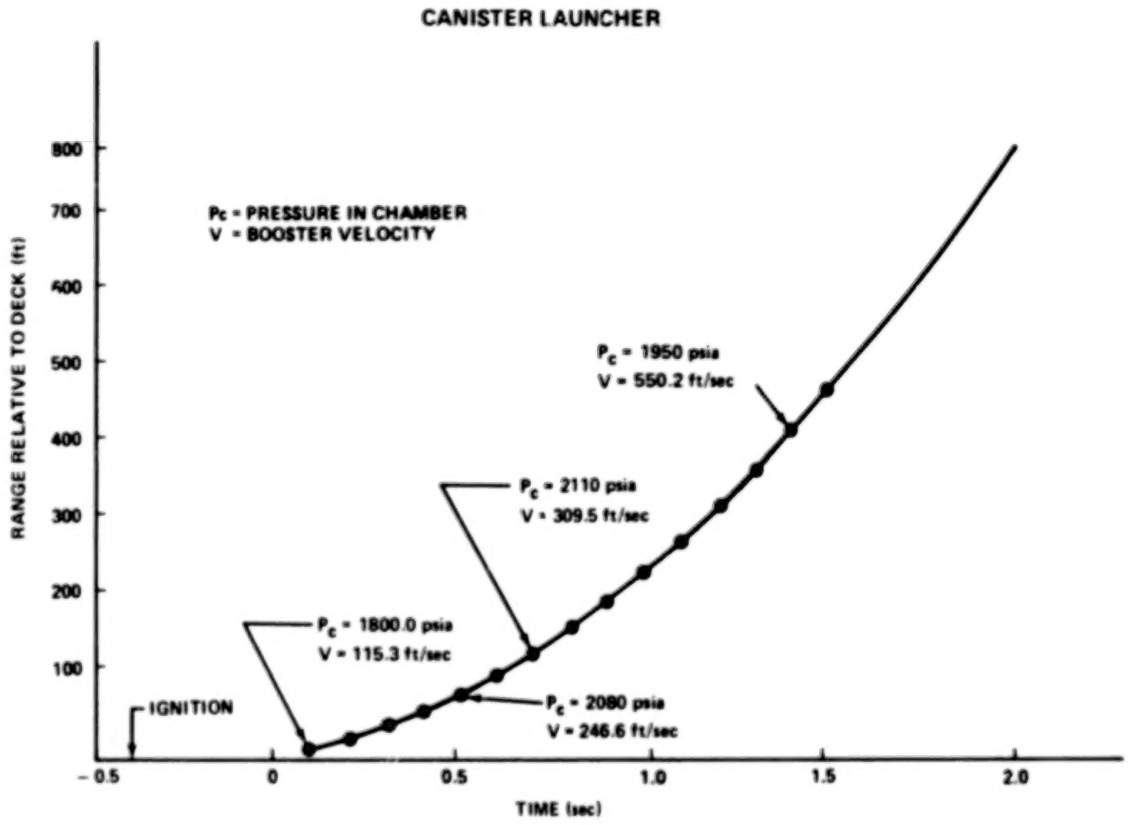

Figure 1. HARPOON booster trajectory.

and pressure depend on the chemical composition of the propellant and the Gibbs free energy of the chemical species. To illustrate this, consider the following arbitrary reaction, j, with chemical species A, B, C, and D; their concentration will be determined by the equilibrium constant K_j, where

$$K_j = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad . \tag{1}$$

For reaction j,

$$aA + bB \rightleftharpoons cC + dD \quad . \tag{2}$$

TABLE 5. RESULTS FROM THERMOCHEMICAL ANALYSIS (ONLY CONCENTRATIONS FOR GASEOUS SPECIES)

Concentrations[a] at 1-D Exit Plane (ppm) Pressure (psia) — Temperature (K)							
Species	1800-3229	1870-3232	1930-3234	1960-3235	2000-3236	2080-3238	2110-3239
Cu	6.0475+2	5.8093+2	5.6194+2	5.5288+2	5.4126+2	5.1936+2	5.1156+2
CuO	1.3782+0	1.3224+0	1.2780+0	1.2568+0	1.2297+0	1.1787+0	1.1604+0
AlCl	1.2570-2	1.2289-2	1.2061-2	1.1950-2	1.1809-2	1.1537-2	1.1438-2
$AlCl_2$	1.1298-1	1.1268-1	1.1244-1	1.1232-1	1.1217-1	1.1187-1	1.1175-1
$AlCl_3$	1.0376+0	1.0563+0	1.0720+0	1.0797+0	1.0900+0	1.1101+0	1.1175+0
AlOCl	8.4671-2	8.2805-2	8.1293-2	8.0561-2	7.9621-2	7.7819-2	7.7163-2
AlO_2H	2.2437-2	2.1935-2	2.1529-2	2.1332-2	2.1080-2	2.0596-2	2.0420-2
CN	4.174-7	4.243-7	4.301-7	4.329-7	4.367-7	4.441-7	4.468-7
CO	1.0746+5	1.0745+5	1.0743+5	1.0743+5	1.0742+5	1.0747+5	1.0740+5
COCl	3.3739-2	3.4341-2	3.4847-2	3.5096-2	3.5427-2	3.6076-2	3.6315-2
$COCl_2$	1.193-5	1.238-5	1.276-5	1.296-5	1.321-5	1.373-5	1.392-5
CO_2	1.0007+5	1.0009+5	1.0010+5	1.0011+5	1.0012+5	1.0013+5	1.0014+5
Cl	2.1589+2	2.1150+2	2.0794+2	2.0622+2	2.0399+2	1.9973+2	1.9819+2
ClCN	8.979-6	9.315-6	9.603-6	9.747-6	9.939-6	1.032-5	1.047-5
Cl_2	4.7017-1	4.6951-1	4.6899-1	4.6872-1	4.6840-1	4.6775-1	4.6749-1
HCl	1.8237+5	1.8238+5	1.8239+5	1.8239+5	1.8239+5	1.8240+5	1.8240+5
HCN	1.0504-2	1.0905-2	1.1249-2	1.1421-2	1.1650-2	1.2108-2	1.2280-2
H_2S	2.6441+5	2.7126+2	2.7698+2	2.7981+2	2.8351+2	2.9078+2	2.9346+2
NH_3	5.2735-1	5.4782-1	5.6536-1	5.7413-1	5.8582-1	6.0920-1	6.1798-1
NO	1.3875+0	1.3581+0	1.3342+0	1.3226+0	1.3078+0	1.2792+0	1.2689+0
NO_2	2.771-6	2.708-6	2.658-6	2.633-6	2.601-6	2.541-6	2.519-6
SO	5.1139+1	5.3373+1	5.2735+1	5.2421+1	5.2009+1	5.1204+1	5.0907+1
SO_2	4.7992+2	4.7336+2	4.6787+2	4.6518+2	4.6164+2	4.5471+2	4.5216+2
SO_3	1.7469-3	1.7210-3	1.6994-3	1.6888-3	1.6750-3	1.6479-3	1.6379-3
CuCl	1.9666+1	1.9279+1	1.8948+1	1.8792+1	1.8591+1	1.8207+1	1.8067+1

a. 6.0475+2 = 6.0475E+2

The values in the brackets are the partial pressures for the species. The a, b, c, and d in equation (2) are the stoichiometric coefficients or the number of molecules of each species.

The equilibrium constant K_j is related to the Gibbs free energy of the standard state for each chemical species by equation (3):

$$K_j = e^{-\Delta G/kT} \quad , \tag{3}$$

where

$$\Delta G = cG_C + dG_D - aG_A - bG_B \quad . \tag{4}$$

The G is the Gibbs free energy at the temperature in question for the standard state of the chemical species.

In the actual combustion chamber many reactions occur concurrently. Some are competing reactions which require some of the same species as a reactant. The thermochemistry program simultaneously calculates the concentrations of the many possible species by minimizing the Gibbs free energy for the combustion chamber under equilibrium conditions. Thus, the chemical species computed in the one-dimensional equilibrium thermochemistry program depend on the chemical composition of the propellant and the chemical compounds in the program data base. The thermochemical data for compounds listed in Table 3 were the basic set of data which determined the various chemical species that can exist in the simulated HARPOON motor.

In actual practice, one must consider all potentially applicable chemical species. However, because the computer program is limited to handling 100 species, those species with molecular fractions less than 10^{-10} are deleted. Nevertheless, one must always prove that the deletion of a species had no significant effect on the concentrations of the other species in the system.

A small study was conducted by omitting species that had negligible concentration in a run and reinserting species that had been previously omitted. No species concentration changed, thus proving the validity of the technique.

The concentration of the species depends on the equilibrium constant K, which is dependent on the temperature via equation (5):

$$\frac{d \ln K}{dT} = \frac{H}{RT^2} \quad , \tag{5}$$

where H is the enthalpy of the reaction being considered [7]. Consequently, it is not critical that one investigate the impact of various pressure chambers. It is noted from Table 5 that the temperature increase is 10 K over the entire chamber pressure range. This small increase in temperature causes a corresponding small increase in concentration of a few species.

In Paragraphs III.B and III.C, an error analysis of the resulting species and their concentrations will be presented. However, before the error analysis is discussed, the source of the thermodynamic data used together with its accuracy should be explained. The thermodynamic data needed to calculate the gaseous chemical species in the plume are readily computed via partition functions from spectroscopic constants. The thermodynamic properties of liquids and solids must be obtained from experimental measurements. The thermodynamic properties are normally expressed as functions of the internal partition function Q, i.e.,

$$\frac{C_P^{\,o}}{R} = \frac{T^2 d^2 \ln Q}{dT^2} + \frac{2T d(\ln Q)}{dT} + \frac{5}{2} \quad , \tag{6}$$

where the superscript o is standard state of the heat capacity at a constant pressure C_p, R is the universal gas constant, and T is the temperature. Then,

$$\frac{S_T^{\,o}}{R} = \frac{T d(\ln Q)}{dT} + \ln Q + \frac{3}{2} \ln M + \frac{5}{2} \ln T + S_c + \frac{5}{2} \tag{7}$$

where S is the entropy and M is the number of molecules,

$$\frac{H_T^{\,o} - H_0^{\,o}}{RT} = \frac{T d \ln Q}{dT} + \frac{5}{2} \tag{8}$$

where H_T is the enthalpy at a temperature, and

$$\frac{-\left(G_T^{\,o} - H_0^{\,o}\right)}{RT} = \frac{S_T^{\,o}}{R} - \frac{\left(H_T^{\,o} - H_0^{\,o}\right)}{RT} = \ln Q + \frac{3}{2} \ln M + \frac{5}{2} \ln T + S_c \tag{9}$$

where G_T is Gibbs free energy at a temperature and

$$S_c = \ln k \left(\frac{2\pi k}{N_O h^2}\right)^{3/2} \quad .$$

The internal partition function Q is represented as

$$Q = \sum_{m=1}^{L} Q^m \tag{10}$$

where Q^m is the internal partition function for the mth electronic state and L is the number of electronic states.

The molecular partition function Q^m is described in equation (11):

$$Q^m = Q_e^m Q_v^m Q_r^m Q_P^m Q_\theta^m Q_\omega^m Q_c^m \quad , \tag{11}$$

where Q_e^m, Q_v^m, and Q_r^m are the electronic, vibrational (harmonic oscillator), and classical rotational contributions. The other quantities are as follows: rotational stretching, Q_P^m; low temperature rigid rotation, Q_θ^m; Fermi resonance, Q_ω^m; and both anharmonic and rotation interaction, Q_c^m, are corrections. The last four terms are correction terms for various interactions not considered classically. Partition functions are classically thought of as a way to partition the internal modes of energy into rotation, vibration, and electronic modes. These energy modes are coupled and depend on each other.

The partition functions themselves can be calculated very accurately for a given electronic, vibrational, and rotational state, but molecules of particular temperatures will contain many electronic, vibrational, and rotational states. Thus, techniques for terminating the terms used in the calculation of the thermodynamic properties have been developed [8,9].

B. Error Analysis of Atomic Species

The uncertainty of the thermodynamic properties of the atomic species is now considered by examining the spectroscopic equation governing these thermodynamic characteristics.

In a monatomic molecule, the electronic energies are the only internal energy contributions; therefore, equation (10) applies only to the electronic contributions. The use of the electronic states to compute the entropy (S^o), heat capacity (C_p), and enthalpy (H) for the atomic species is limited by determining the number of electronic states to be considered. At the temperature considered in the HARPOON combustion chamber (≤ 3000 K), the thermodynamic properties are accurately described, because many upper electronic states are not heavily populated at these temperatures. In some atoms, such as Cr, there are many electronic states to consider, although, again, at these temperatures this does not present a problem. The excited electronic states are also fairly well known for atoms. An error of 10 percent is considered an upper limit for the thermodynamic properties for any atomic species.

C. Error Analysis of Diatomic and Polyatomic Species

The spectroscopic constraints for the vibrational, rotational, and correction terms are not as well known as for electronic states. This is particularly true when these properties must be determined at many different excited electronic states for an infinite list of compounds. In all cases the correction terms are included in the Joint-Army-Navy-NASA-Air Force (JANNAF) tables. If the spectroscopic constants were not known for specific compounds, they were estimated from analogous works with similar compounds. There are also some errors in assignment of states by different researchers. The errors for these compounds are listed in Table 6 for entropy, enthalpy, and spectroscopic constants; an overall error estimate is also given.

D. Summary of Error Analysis

The analysis of errors in the thermodynamic data is straightforward in many cases but somewhat subjective in others. In general, the overall error approximation reflects the highest error for a particular thermodynamic parameter. Since the parameters are all interrelated, errors tend to propagate through all of the parameters. It should be noted that these are probably worst-case error bounds. The error in NH_2 is the most severe. The values which are

TABLE 6. ERROR ANALYSIS

Species	S^o (%)	ΔH_f^o at 298 K (%)	Dissociation Energy, D_o (%)	Vibrational Levels, V_i (%)	Appropriate Overall Error (%)	Comments
AlCl		8			8	
$AlCl_2$	<1	7			7	
$AlCl_3$	1.3	<1			1	
AlO		12	1.6		12	
AlO_2	3.4	11.3			10	
AlO_2H	2.5				5	
AlOH	1.0	7			7	
Al_2O	2.4	16	1.6	15.8 V_1	16	
Al_2O_2	6.0	9.6			9.6	
$Al_2O_3(S)$	<1	<1			1	Very well studied
$Al_2O_3(L)$						
C ClO		66			66	
Cl					5	Molecule studied in great detail but many higher electronic states
Cl_2					3	Some errors in electronic states
Cl_2O		2.8			2.8	
Cr	<1	1			5	Many electronic states to consider
Cu(L)					1	Very well studied
Cu		<1			10	Many electronic states and heat of sublimation 10 percent off
Cu_2		<1			10	
CuO	<1	13.8			13.8	Poor electronic assignments
H					1	Very well studied
HN		4			4	
SH		3.6			5	Analogous molecular parameters used
H_2					1	Very well studied
H_2N		3.2			30	Higher H_f values could be off by factor of three
H_2O					1	Very well studied

TABLE 6. (Concluded)

Species	S^o (%)	ΔH_f^o at 298 K (%)	Dissociation Energy, D_o (%)	Vibrational Levels V_j (%)	Appropriate Overall Error (%)	Comments
H_2O_2					1	Very well studied
H_2S		4.8			5	Well Studied
NH_3		1			1	Very good data
NO		<1			1	Very few electronic states
NO_2		2.5			2.5	
N_2					1	Very good data
N_2O		<1			1	Very good data
O					1	Very good data
O_2	<1				1	Very good data
SO	<1	25			20	All other data fairly good
SO_2	<1	<1			1	Good data
SO_3					1	
S	<1	<1			1	
S_2		<1			1	
OH		3			3	Some errors below 400 K
CO_2	<1	<1			1	
COS		<1			1	Accurate spectroscopic data
CN	<1	2.4			2.4	Accurate spectroscopic data
NOCl	<1	<1			1	
HCl		<1			1	Accurate spectroscopic data
CuCl		1.8			1.8	
CH_4	<1	<1			1	
CH_3	<1	<1			1	
CH_2O	<1	5.4			5.4	Accurate spectroscopic data
CH_2	1	1			1	
HCO	<1	1.9			1.9	
CO	<1	<1			1	Very well studied
HCN	<1	6.0			6	Fairly good data
AlOCl		6.0			6	Fairly good data

calculated using spectroscopic data are, in general, accurate. For liquids and solids, the data can be measured only experimentally, and usually larger errors are found. It should be noted that it is generally agreed that the calculation of thermodynamic properties via partition functions is as accurate or more accurate than allowable experimental errors. Generally, the errors are small and should give small errors in concentrations. Errors in concentration of 100 percent should be considered extreme cases and then only as a margin of safety for potentially hazardous species at high dosages. This condition is true because of the relationship

$$\frac{-\Delta G_T}{2.302\,RT} = \log_{10} K_p \quad ,$$

where ΔG_T is the Gibbs free energy difference between reactants and products and K_p is the equilibrium constant of the chemical reactions at equilibrium. K_p is the ratio of the concentrations of the reactants and products. The log term magnifies any error in ΔG_T, but all G_1 must be in error in opposing directions for serious errors to present complications. As a result of the many competing reactions, serious errors in certain species become diluted to some degree. The data for error analyses came from the JANNAF Thermochemical Tables, Volume I, II, III, and IV and their references [10].

Thus, the species listed in Table 5 will be the basis of the next step in the analysis.

IV. SOLID ROCKET MOTOR NOZZLE AND PLUME ANALYSIS

The assumptions and resultant species for the nozzle and plume are presented in this section. The results obtained in Section III are used as the inputs to this analysis.

The assumption and theoretical analysis are very important in arriving at the species and their concentrations in the plume for the following reasons. First, in the chamber analysis the system was well defined in that all the constituents and the fluid dynamics involved in the reaction were well defined. However, the constituents and the fluid dynamics of the rocket exhaust plume are not as easily defined. More specifically, air is now entrained into the

plume and shock fronts are set up. Second, very little experimental data on the species have been directly collected and analyzed from a solid rocket motor plume to support the theoretical analysis. This lack of empirical data for the hot exhaust plume exists due to the complexities of obtaining meaningful measurements from the plume. Therefore, the only way to verify the accuracy of the analyses techniques utilized in this study is that the performance of a solid rocket motor, which depends on the species present and their concentration, can be predicted to a high degree of confidence. Secondary techniques have been used (e.g., sampling the stabilized exhaust cloud) which afford indirect verification of the analysis; however, this sampling provides only a coarse verification at best.

A. Background of Analysis Logic

The order of our analytical procedure for a solid rocket motor was to first perform a one-dimensional thermochemical analysis and then use the results of that analysis as the basis for a two-dimensional nozzle thermochemical and aerodynamic analysis. For solid propellants with aluminum in the formulation, a two-dimensional, two-phase nozzle analysis is required. Since our primary interest is in the species in the plume (and since good plume experiments do not exist), we must use indirect verification from a solid rocket motor performance analysis for an indication of species concentration accuracy.

Figure 2 shows the schematic used for the motor, nozzle, and plume analysis. The first portion of the figure shows the solid propellant motor burning at some chamber pressure, P_c, and at chamber temperature, T_c, and some of the principal (but not necessarily all) species of interest that are formed in the combustion process. This combustion analysis is valid up to the nozzle throat, where two-dimensional effects start. From the throat to the nozzle exit plane, a two-dimensional, two-phase nozzle analysis is utilized. From the nozzle lip downstream, a region exists which is primarily controlled by the mixing of the ambient air, and chemical reactions which are occurring at a finite rate are analyzed. Therefore, we have to perform a finite-rate mixing and afterburning analysis.

B. Analysis of Losses

The losses considered in the investigation are given in Table 7. The normal nozzle losses (divergence, two-phase flow, and changes in the temperature and pressures in the nozzle) affect the species. The boundary layer loss

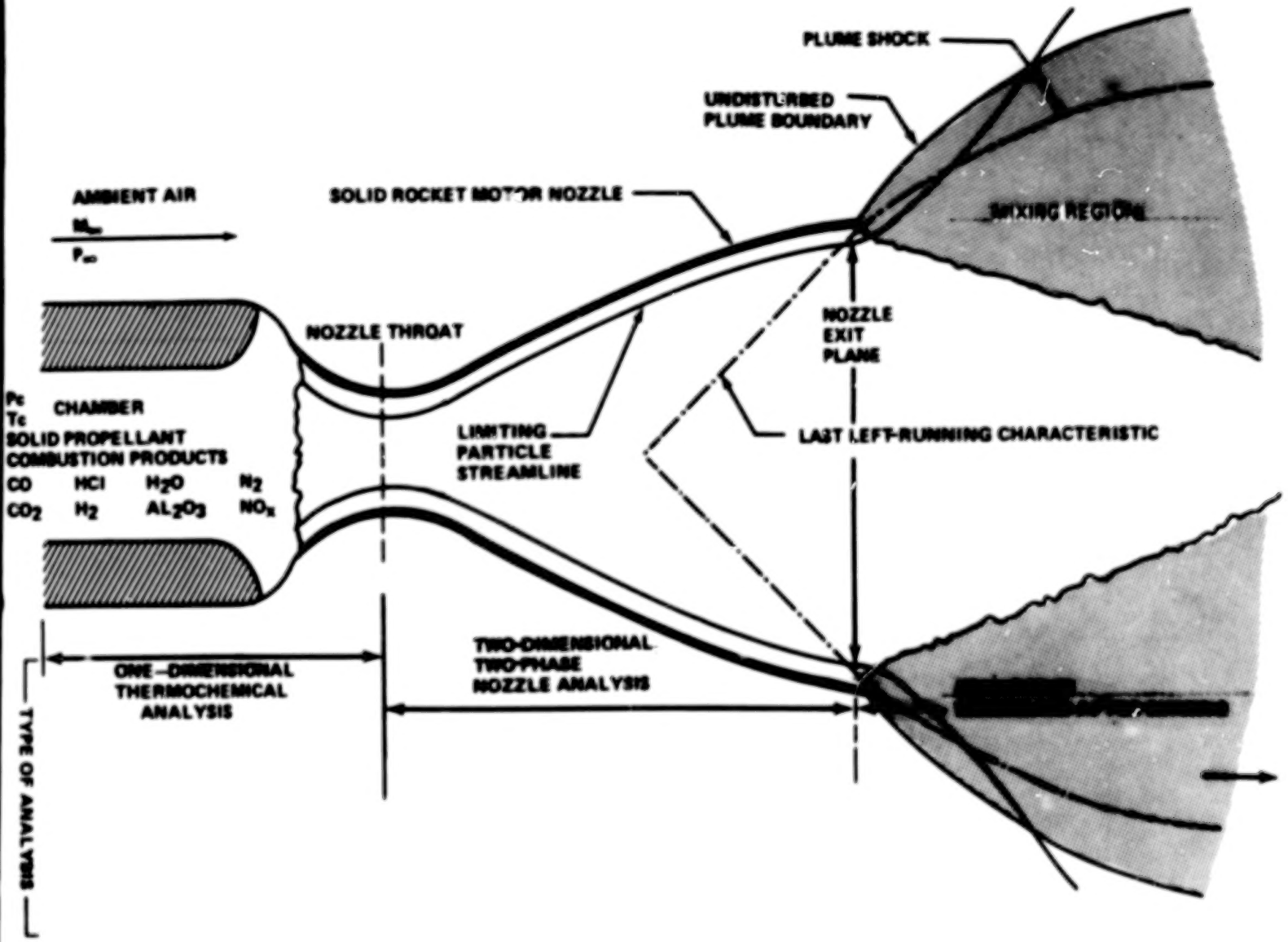

Figure 2. Solid rocket motor, nozzle, and plume.

TABLE 7. LOSSES CONSIDERED BY PERFORMANCE ANALYSIS

• Divergence	Two dimensionality of nozzle
• Two Phase	Velocity and temperature lag of particles
• Boundary Layer	Effect of friction and heat transfer
• Energy Release	Coupled C^* (subsonic)
• Submergence	Nozzle entrance effects
• Kinetic	Chemical nonequilibrium
• Combustion in Nozzle and Plume	Afterburning

analysis determines the inviscid contour that is analyzed; the energy release loss is an indication of the combustion efficiency of the motor. The kinetic loss is an indication of the rate of reaction in the nozzle. In the case of the HARPOON booster, the motor is operating at high chamber pressures on the order of 1800 to 2100 psi [11], and kinetics is not an important factor. When the flow is expanded in the plume, the pressure and temperature drop rapidly. The kinetics of the reactions in the plume are important, and a finite-rate mixing and after-burning analysis is required. A loss that is not considered but which does occur in some motors is the loss due to nonuniform entrance conditions. Since the HARPOON grain is axisymmetric and has a conventional design, this loss need not be considered in the particular case of the HARPOON. A variety of analysis tools is available (Table 8). The variety of one-dimensional programs gives an indication of the losses and generates input to the two-dimensional programs. The results of the two-dimensional programs are then fed back to the one-dimensional programs to get species concentrations. These species and exit conditions are used as input to the low altitude plume program (LAPP) code for an afterburning analysis.

Table 9 gives the input requirements of the two-phase nozzle analysis program. A chemistry model has to be chosen, physical constraints (e.g., the nozzle contour and external ambient conditions) must be determined, and the particle size and mass flow distribution must be chosen. The other parameter requirements are usually set and are not changed from case to case.

1. Losses Due to Two-Phase Flow. An important consideration is where to perform a one- or a two-phase flow analysis. One-phase flow means that the rocket exhaust can be treated as containing only gaseous species, whereas two-phase flow means that rocket exhaust must be treated as being composed of both gaseous and solid species.

TABLE 8. ANALYSIS TOOLS AVAILABLE

• ODE	One-dimensional theoretical equilibrium performance
• OD2P	One-dimensional, two-phase perfect gas nozzle analysis
• ODK	One-dimensional, one-phase real gas kinetic nozzle analysis
• OD2PK	One-dimensional, two-phase real gas kinetic nozzle analysis
• TDE	Two-dimensional, one-phase real gas nozzle analysis
• TPKNA	Two-dimensional, two-phase real gas nozzle analysis
• TDK	Two-dimensional, one-phase real gas kinetic nozzle analysis
• TBL	Turbulent, compressible boundary layer analysis
• AGP	Thermodata preparation
• SCR	Two-dimensional, two-phase, real gas nozzle analysis
• LAPP	Plume afterburning

TABLE 9. TDDD[a] INPUT REQUIREMENTS

Chemistry

- Frozen (ideal gas)
- Equilibrium
- Equilibrium/frozen
- Finite rate

Physical Constraints

- Nozzle contour and external conditions

Particle Information

- Size and mass flow distributions (enthalpies, C_p, heat of formation (JANNAF)
- Density

Gas/Particle Interface Data

- Drag coefficients
- Heat transfer coefficients

a. Two-dimensional, two-phase nozzle analysis program

Samples collected at rocket firings (Fig. 3) clearly show the presence of aluminum oxide [12].

As can be seen, a number of spheres of varying size have been collected. The largest particle seen at this test was on the order of 20 μm in diameter; the smallest particles, which are small white dots seen alone on the figure and

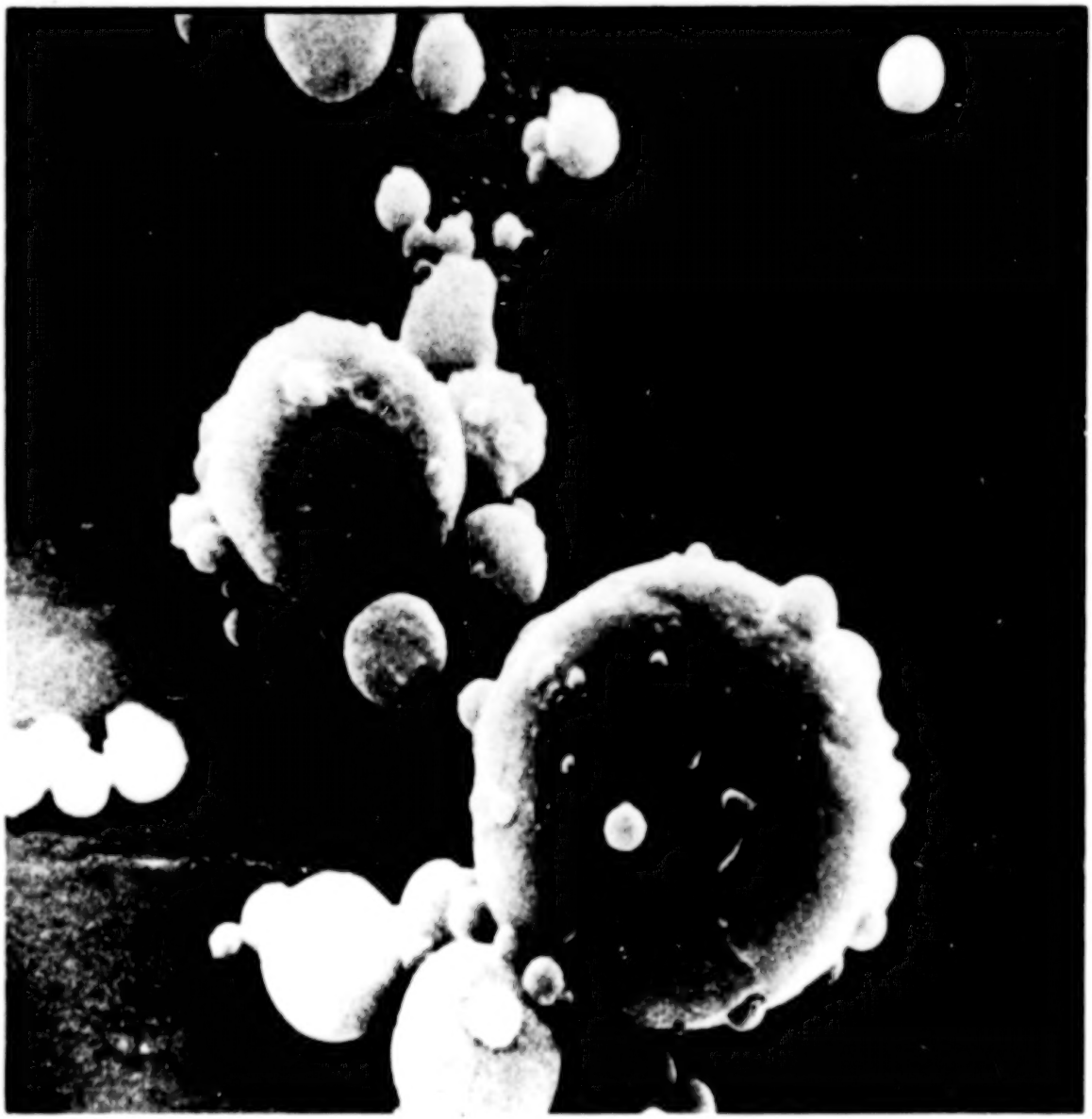

Figure 3. Electron microscope of aluminum oxide particles.

occasionally on the larger particles, are approximately 0.1 μm in diameter. These small particles (alpha aluminum oxide) are spherical; even the larger ones which appear hollow are spherical in shape. In Figure 4 one can observe a white fuzz aluminum oxide on top of the alpha aluminum oxide (60 μm diameter). This white fuzz material is an example of gamma aluminum oxide which results from some small solid rocket firing and probably would not be found in the large HARPOON booster [12].

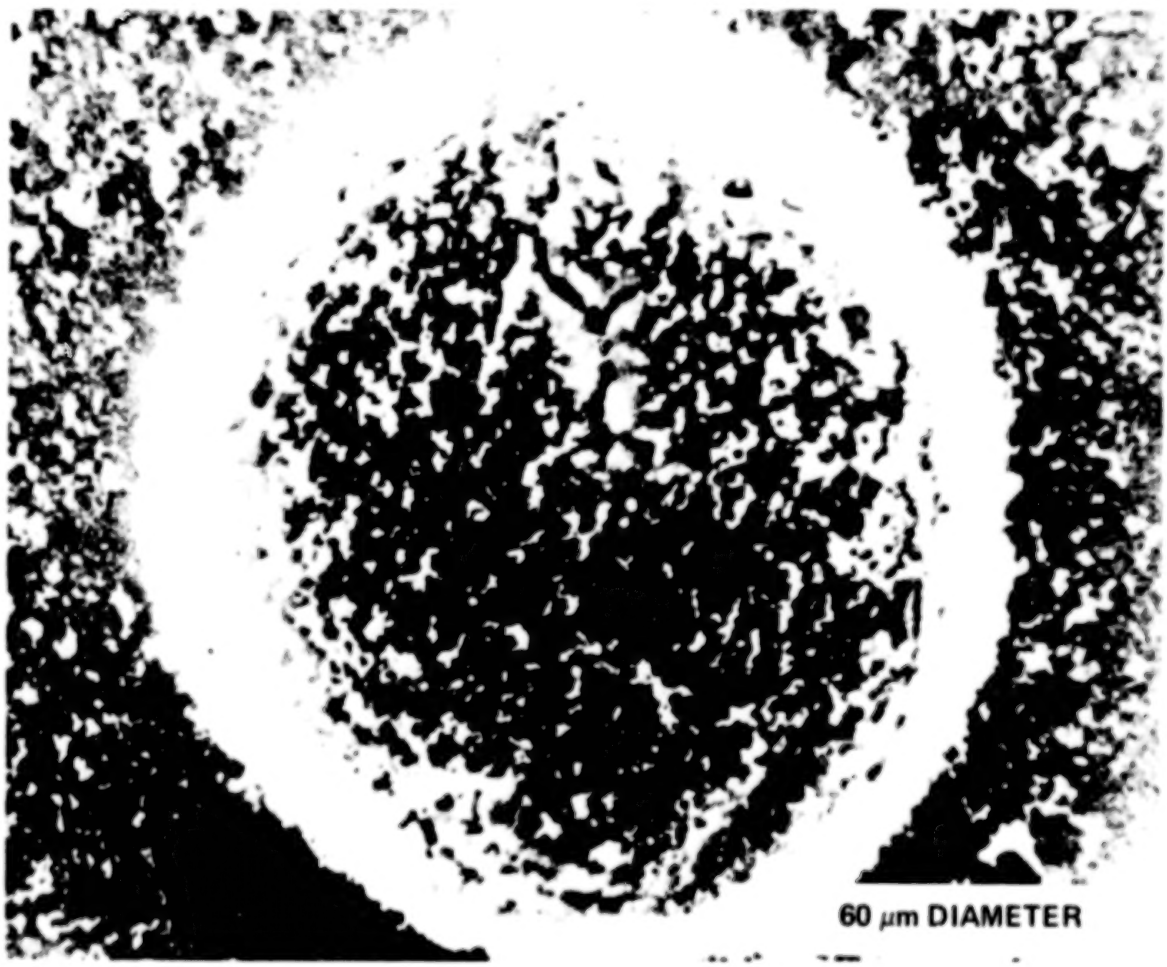

Figure 4. Gamma aluminum oxide particles.

The determination of the size, type, and distribution of the aluminum oxide is of primary importance to the analysis. The basic assumptions that are made for particle flow are given in Table 10. The assumption of a spherical particle is probably good since this is typically what is seen in our samples. All the other assumptions are standard. The analysis does not look at every particle. Only a small number of discrete particles are analyzed, and a representative size and weight flow of each of these particle sizes is chosen. At the present time we can consider 10 different particle sizes.

TABLE 10. BASIC ASSUMPTIONS FOR PARTICLE FLOW

- The particles are spherical in shape.
- The particle internal temperature is uniform.
- The gas and particles exchange thermal energy by convection and radiation (optional).
- The gas obeys the perfect gas law.
- The pressure of the gas and the drag of the particles contribute to the force acting on the control volume.
- The gas is inviscid except for the drag it exerts on the particles.
- There are no particle interactions.
- The volume occupied by the particles is negligible.
- There is no mass exchange between the phases.
- A discrete number of particles, each of different size or chemical species, is chosen to represent the actual continuous particle distribution.
- The particles are inert.

The average aluminum oxide particle diameter plotted against throat diameter in inches for various aluminum levels from 14 to 20 percent is shown in Figure 5. The majority of the data is at 16 percent aluminum, which includes Titan, Minuteman, and Polaris type motors. From intuition and some preliminary data, the HARPOON particle size was chosen to be approximately 12 μm diameter for a 2.23 in. throat diameter.

2. Two-Dimensional Losses. For a two-dimensional nozzle analysis, the nozzle must be modeled in great detail. Figure 6 shows all the various angles and physical parameters that are required for valid analysis.

There are two primary techniques which can be used to analyze two-dimensional, two-phase nozzles: the mesh point technique, which was written by Kliegel and Nickerson at TRW Systems in the early 60's, and the streamline normal technique, which was developed in the mid-60's [13]. For this particular analysis, the mesh point construction method of Kliegel and Nickerson was chosen. Figure 7 shows a schematic of the calculation technique. The nozzle is analyzed by having a finite difference mesh which is calculated repetitively from the initial value line to the exit of the nozzle. Knowing the

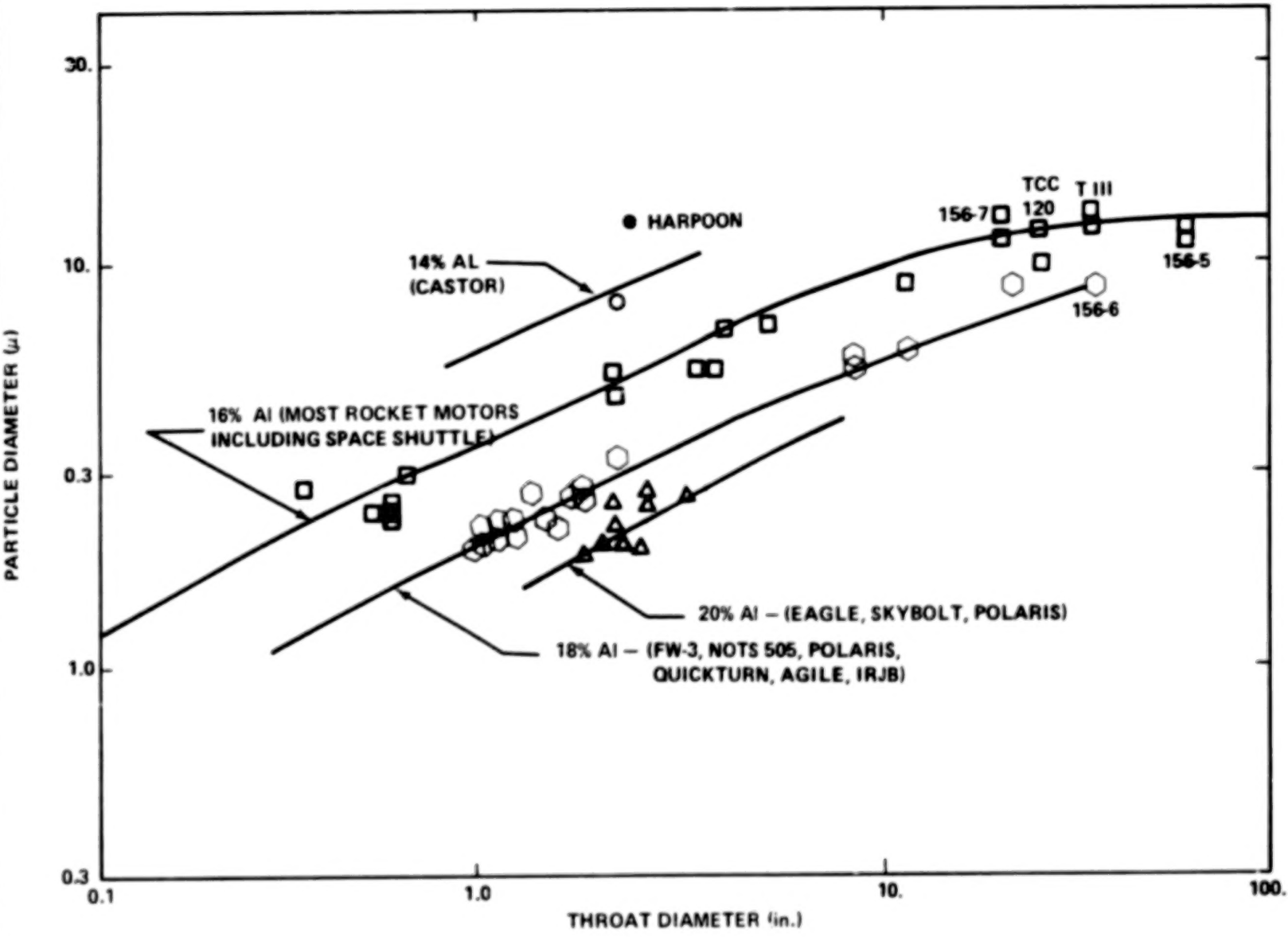

Figure 5. Aluminum oxide particle diameter versus throat diameter.

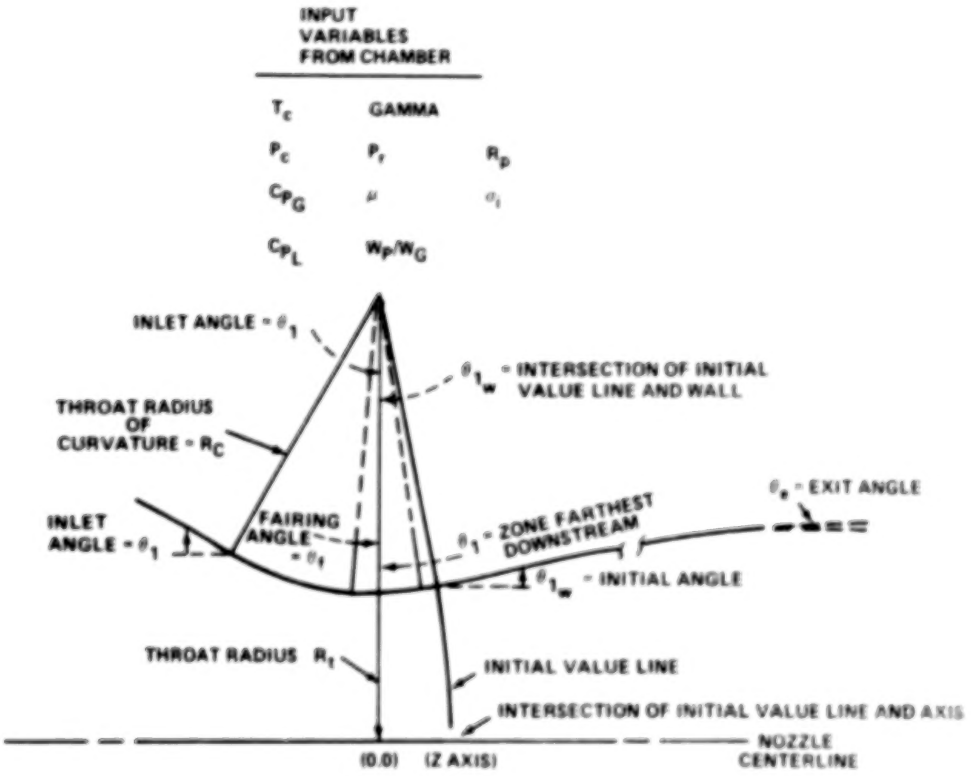

Figure 6. Nozzle parameters.

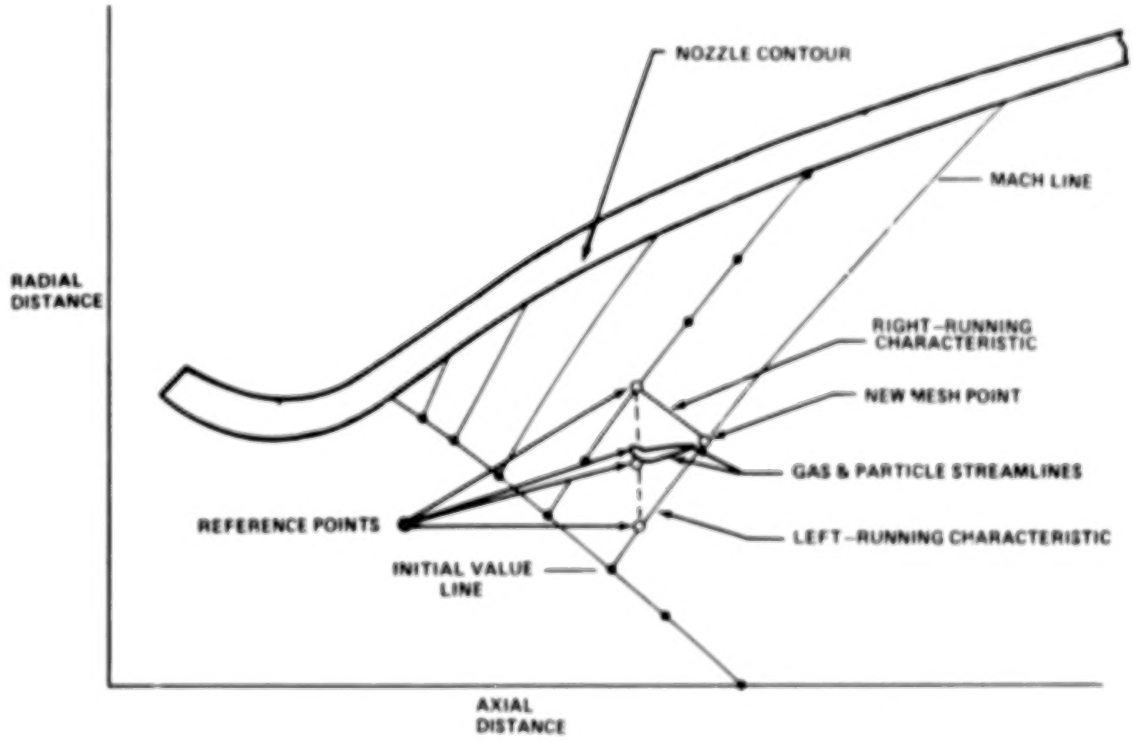

Figure 7. Calculation technique schematic.

values of the flow variables and the species at two reference points, the value of all the parameters can be calculated at a third point which is the intersection of the cones of influence of these two reference points.

The schematic of the thermochemistry table construction is shown in Figure 8. The table is constructed using the data given in Table 5. Since the two-phase nozzle flow is nonequilibrium and dissipative, the stagnation pressure at every point in the nozzle is different; therefore, if the species are to be calculated, a table which uses two calculable properties as independent variables

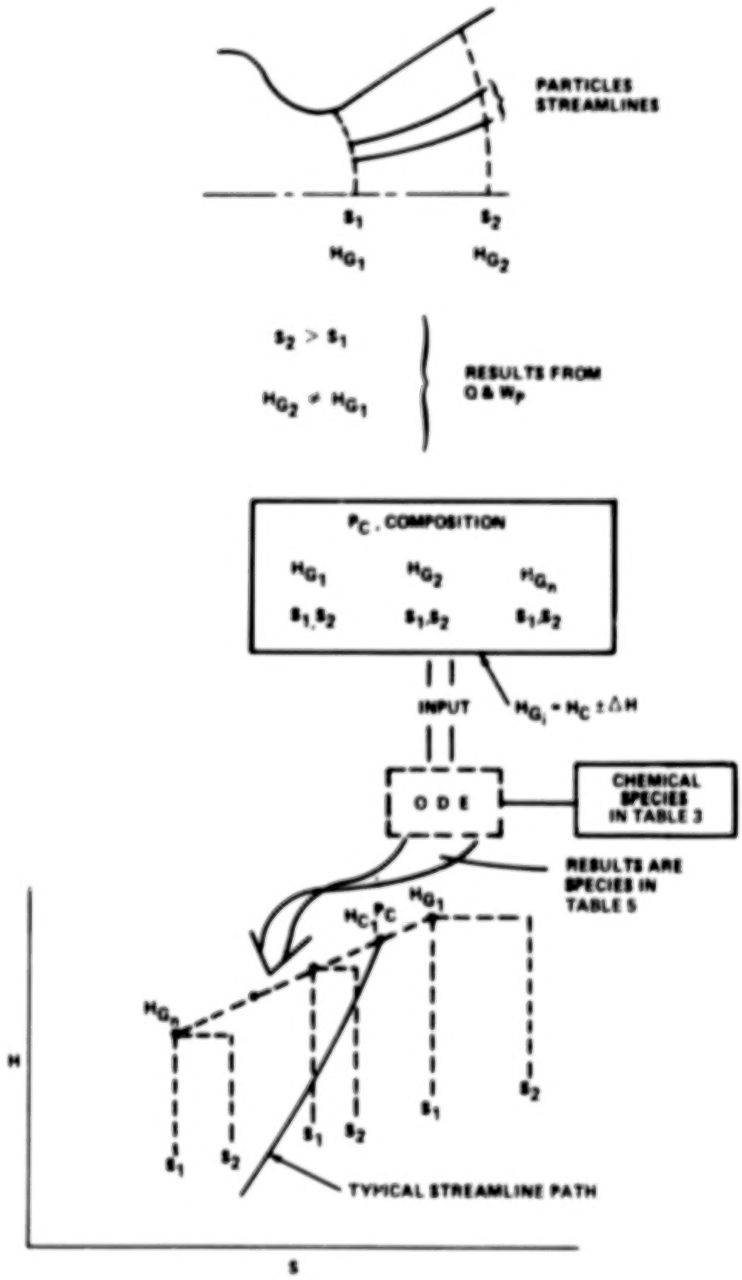

Figure 8. Schematic of thermochemistry table construction.

must be constructed. The present technique uses enthalpy and entropy. Knowing the enthalpy and entropy of any field point in the nozzle and utilizing a table look-up routine for the calculated stagnation pressure, the species at that static pressure can be determined. The species concentration determined by this technique may or may not be significantly different, but it has more validity than the value determined from a one-dimensional equilibrium calculation or a single variable table look-up routine.

The results of this type performance analysis are presented in Table 11 for seven motors (four NASA and three Navy motors) [14]. The three Navy motors tested were involved in the C-4 program. With the exception of the LS-2 motor, which had difficulties because of nozzle erosion, all of the analyses of the performance are within ±0.5 percent. This is certainly adequate and is a good indication that the species calculations are valid.

TABLE 11. PERFORMANCE ANALYSIS RESULTS

Motor Parameters	FW-4	Jupiter Orbiter	JPL-ATS	Old Surveyor	LS-1	LS-2	DEMO-1
Geometry							
ϵ	47.4	80	35	46.22	14.8	14.7	10.56
R_T – in.	1.16	0.7245	2.04	1.765	2.07	2.07	2.02
Re/ft	2.0	1.5	3.0	2.1	4.0	4.0	4.0
θ_{max} – deg	28.0	30.0	26.0	34.0	25	25	26
θ_{exit} – deg	20.0	11.6	10.0	20.49	19	19	23
$\Delta\theta$ – deg	0.0	18.4	16.0	13.51	6	6	3
L – in.	19.17	15.57	31.83	21.18	15.8	15.8	11.85
Ballistics							
P_c – psia	794	143	200	511	778	950	1003
T_c – °R	6017	5827	5654	6008	6305	6305	6305
C* – ft/sec	5169	5164	5097	5195	5288	5288	5288
I_{vac} at ϵ – sec	315.3	324.6	306.4	319.9	301.38	301.8	293.21
w_p – lb/sec	19.94	1.55	17.06	31.60	66.24	80.7	80.64
Performance							
ΔIs 2D-2P-sec	29.95	37.05[a]	15.96	25.89	23.92	22.4	23.97
ΔIs ER – sec	3.75	9.74	3.45	10.24	0	0	0
ΔIs KIN – sec	0.0	1.95	1.00	0.0	0.0	0.0	0.0
ΔIs BL – sec	3.15	1.65	5.95	3.52	2.1	2.1	1.87
I_{Vac} pred – sec	287.5	274.2	280.04	280.3	275.36	277.3	267.37
I_{Vac} delivered – sec	286.4	276.0	280.2	279.3	275.2	274.3[b]	267.7
I_{Vac} pred – I_{Vac} del	1.1	-1.8	-0.16	1.0	+0.1	-3.0	-0.33
I deviation	0.35	-0.55	-0.05	0.31	+0.04	-1.0	0.12

a. Loss with single particle size; calculation with particle size distribution showed shocks in nozzle.

b. Silica phenolic exit cone – severe erosion.

As further evidence of the validity of the technique, Figure 9 shows the ratio of chamber pressure to wall pressure versus area ratio for a 16 percent aluminum solid propellant fired in two motors at NASA/MSFC. The data points and error bands are shown as a circle with a band. The analysis shows a good comparison with the data. Another comparative pressure curve is shown in Figure 10 with the same motor fired with a 2 percent aluminum solid propellant. Again, good results were obtained using the analysis technique. Thus, since the HARPOON motor has 6 percent aluminum in the propellant and the analysis has bounded the problem at both the 2 and 16 percent aluminum levels, the accuracy obtained for 6 percent aluminum should be comparable to the first two cases.

To illustrate some of the two-phase phenomena that occur, Figure 11 shows a nozzle flow field for a different nozzle, the Space Shuttle SRB, which is basically a low-altitude nozzle fired with a 16 percent aluminum solid propellant. At the exit of the nozzle the flow expands into a plume. A 10 μm particle, the innermost particle, does not turn with the flow; however, a smaller particle (3 μm) does turn some in the plume. The smallest particle shown is a 1.5 μm diameter particle. It initially shows an expansion and does tend to follow the plume boundary; however, the plume loses density and the ability to turn the particle back. At some point downstream, the small particle actually flows through the gaseous plume boundary. Thus, although calculations may show the plume boundary will not impinge upon a vent or orifice of the ship, particles passing through the plume boundary may actually be impinging or be captured by these ship orifices.

3. Plume Afterburning Losses. The plume afterburning begins at the nozzle exit plane and is a function of the velocity or Mach number of the ambient air (Fig. 12). The air is entrained and finite chemical reactions occur; at some point the mixing layer reaches the nozzle axis, and then fully developed flow occurs downstream of that point. The species, the temperature, and the pressure vary as a function of the amount of mixing. One of the primary uses of this analysis is to determine how much air is entrained into the flow and to determine the dilution factor of the species that occur at the nozzle exit. This, in turn, allows one to determine the kinds of changes in species that occur due to the chemical reactions with the entrained air.

C. Results for the HARPOON Booster Analysis

The HARPOON booster nozzle was analyzed utilizing the two-dimensional, two-phase nozzle analysis program, TDDD [15]. The program was originally written by TRW Systems personnel and has, over the years, been modified by Science Applications, Inc. (SAI) personnel for NASA. The results of the nozzle

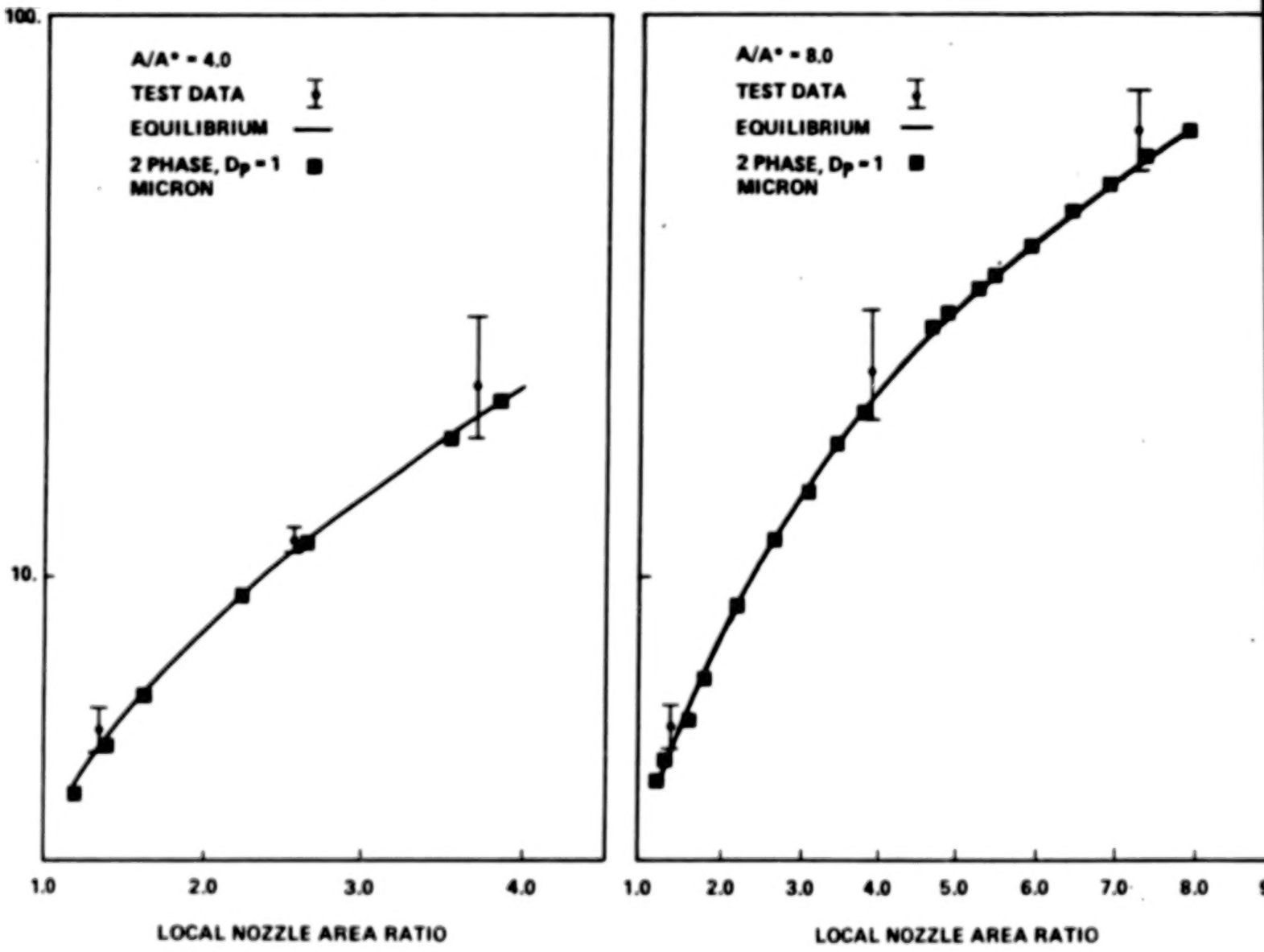

Figure 9. Analytic and experimental nozzle wall pressure, solid rocket 16 percent aluminum oxide.

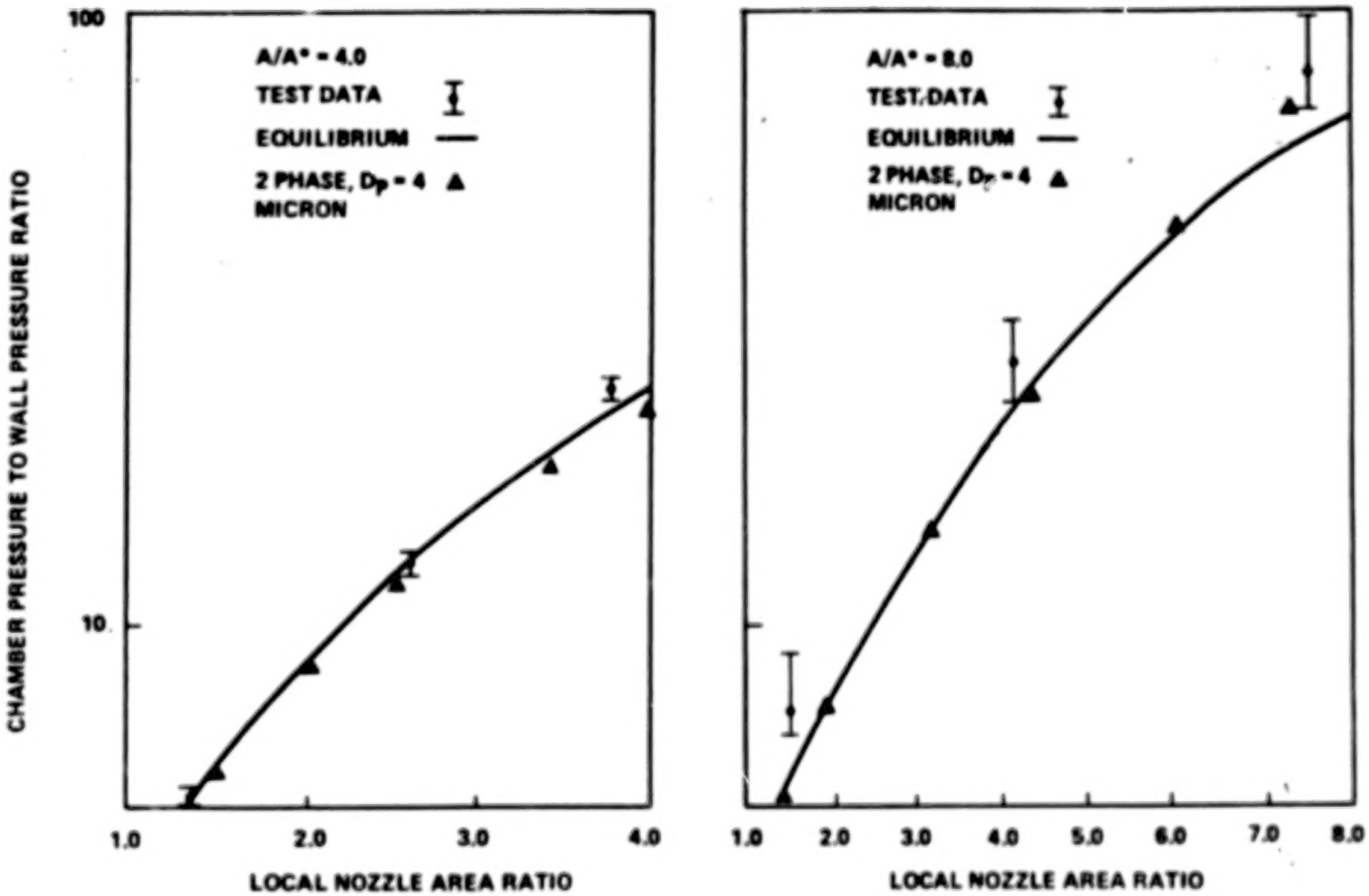

Figure 10. Analytic and experimental nozzle wall pressure, solid rocket 2 percent aluminum oxide.

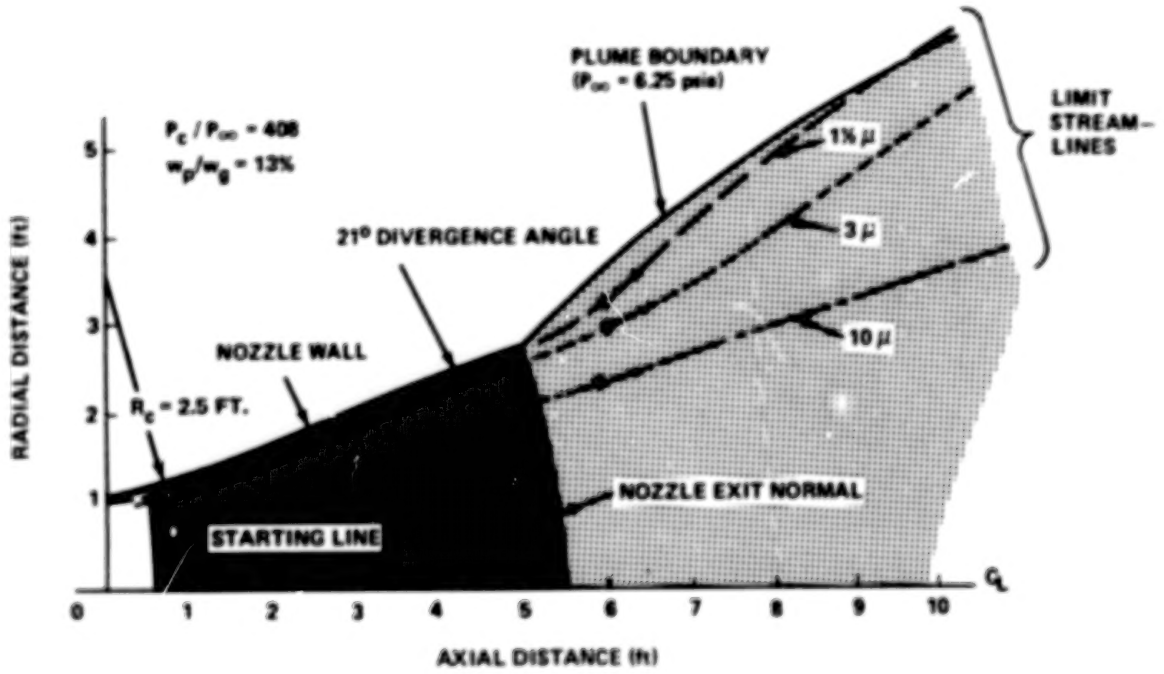

Figure 11. Nozzle-exhaust plume flow fields for a gas-particle system for a P_c/P_∞ = 408.

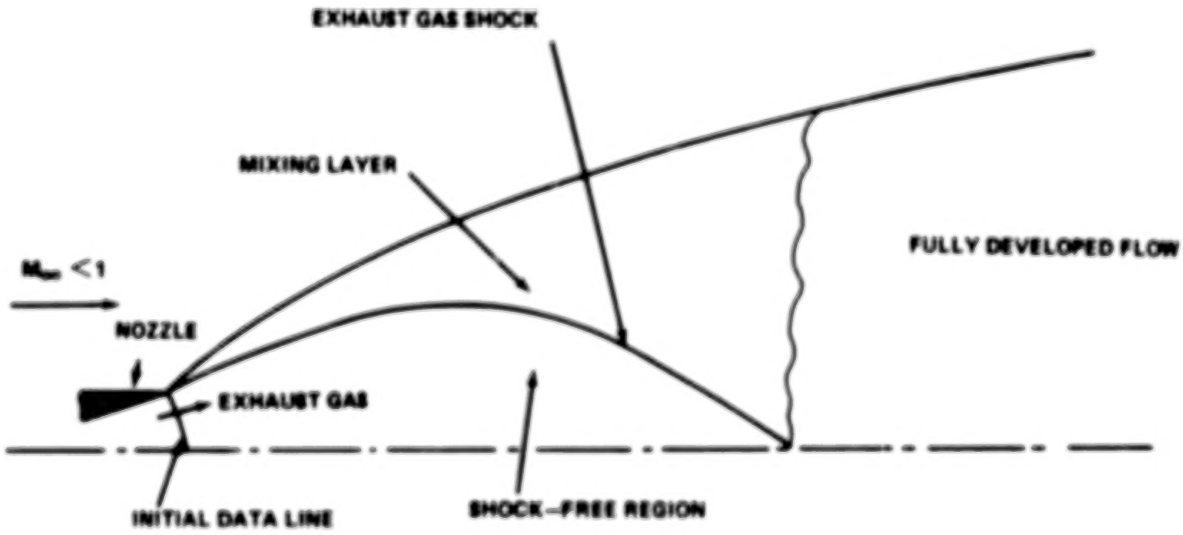

Figure 12. Plume afterburning schematic.

analysis, in terms of static and total pressure at the nozzle exit, were used as input parameters to the equilibrium program. The equilibrium program determined the species present and their concentration (Fig. 12). A range of concentration for each species is shown because the flow in the nozzle is neither uniform nor insentropic because of the two-phase flow. Every point in the flow field has a stagnation pressure which is dependent on the flow history of the particles in the neighborhood of the flow-field point. Due to the nonuniform flow in the nozzle, the static pressure varies radially across the exit plane. These two effects cause a species concentration variation across the exit plane. Table 12 gives the species concentration variation across the nozzle exit plane for the species of interest.

Flow from the nozzle mixes and reacts with the ambient air at a finite rate. The LAPP [16] computer program calculates the amount of air mixed and the species concentrations radially from the nozzle axis to the freestream as a function of distance from the nozzle exit plane. Table 13 lists the finite-rate chemical reactions which are considered by the program for the HARPOON booster exhaust. Table 14 lists the results of the afterburning and mixing analysis. The species concentrations at the centerline of the nozzle and at the edge of the freestream are given for an axial station 120 ft downstream of the nozzle exit. This axial station was chosen because the temperature and velocity at the two radial stations have similar values. The maximum concentration error due to thermodynamic data error is estimated for each species. Figure 13 shows the static temperature of the centerline and edge as a function of distance from the nozzle exit. The edge static temperature rises more rapidly and to a higher value than the centerline. This is to be expected since the edge mixes more rapidly and sooner with the freestream. Figure 14 shows the dilution ratio or the relative amount of air that is entrained by the exhaust as a function of distance from the nozzle exit. Figure 15 shows the plume radial expansion versus distance. General conclusions that can be drawn are that because of the high nozzle exit pressure, 34.73 psia, the plume mixes rapidly with the freestream even at a low vehicle velocity, afterburns near the nozzle exit, and expands and entrains approximately 500 times as much air as the exhaust effluent before the plume dissipates into the ambient atmosphere.

Figure 16 is a photograph of an actual HARPOON missile flight. The photograph has been labeled to indicate some of the important points in the plume. For this particular nozzle, afterburning takes place very close to the nozzle exit. Fully developed flow (i.e., the mixing region between the exhaust and the ambient air extends to the centerline) occurs approximately 20 ft aft of the nozzle exit. Air entrainment is essentially complete and the plume properties are uniform approximately 120 ft aft of the nozzle exit. A point of note is that every motor is different. The analysis performed for the HARPOON is not applicable to other motors; only the analysis technique is transferrable.

TABLE 12. SUMMARY OF HARPOON BOOSTER EXHAUST SPECIES CONCENTRATIONS (ppm)

At Nozzle Exit Chamber Pressure = 1800 psia t = 0.1 sec			
Cu	950 - 5480	ClCn	0.00001 - 0.0006
CuO	3 - 232	Cl_2	0.6 - 17
AlCl	0.03 - 12	HCl	176 900 - 182 250
$AlCl_2$	0.2 - 29	HCN	0.01 - 0.09
$AlCl_3$	1.4 - 27	H_2S	30 - 204
AlOCl	0.2 - 52	NH_3	0.5 - 1.6
AlO_2H	0.05 - 30	NO	2 - 280
CN	0.0000007 - 0.0003	NO_2	0.000007 - 0.02
CO	108 950 - 121 340	SO	64 - 149
COCl	0.05 - 2	SO_2	533 - 657
$COCl_2$	0.00001 - 0.0008	SO_3	0.003 - 0.05
CO_2	84 914 - 98 549	CuCl	27 - 77
Cl	305 - 4274	Cr	0.005 - 1172
$Al_2O_3(S)$	4.22×10^7 - 3.21×10^8 $\mu g/m^3$	$Cr_2O_3(S)$	0 - 1.33×10^6 $\mu g/m^3$

TABLE 12. (Continued)

	Cu	CuO	AlCl	$AlCl_2$	$AlCl_3$	AlOCl	AlO_2H	CN
Chamber	4.8305+3	6.6356.2	1.1378+2	1.9219+2	9.0369+1	3.6124+2	2.9097+2	8.076-3
Throat	5.0345+3	4.8609+2	5.5721+1	1.0496+2	6.1948+1	1.9663+2	1.4187+2	2.705-3
1-D Exit Plane	6.0475+2	1.3782+0	1.2570-2	1.1298-1	1.0376+0	8.4671-2	2.2437-2	4.174-7
Last Left Running Characteristic								
Nozzle Axis (1514.8)	5.3163+3	2.3228+2	1.2417+1	2.8688+1	2.6739+1	5.2000+1	2.9842+1	3.036-4
Minimum P_0 (1152.7)	5.4803+3	8.4149+1	1.8047+0	5.2029+0	8.3912+0	9.0293+0	3.9112+0	2.097-5
Nozzle Lip (1649.9)	9.5063+2	2.8557+0	2.6824-2	1.9894-1	1.3793+0	1.7249-1	4.9026-2	7.204-7

	CO	COCl	$COCl_2$	CO_2	Cl	ClCN	Cl_2	HCl
Chamber	1.2888+5	1.4295+1	9.358-3	7.4629+4	1.0313+2	8.486-3	7.1119+1	1.6740+5
Throat	1.2602+5	7.4542+0	4.314-3	7.8771+4	7.8608+3	3.590-3	4.6031+1	1.7152+5
1-D Exit Plane	1.0746+5	3.3739-2	1.193-5	1.0007+5	2.1589+2	8.979-6	4.7017-1	1.8237+5
Last Left Running Characteristic								
Nozzle Axis (1514.8)	1.2134+5	1.9121+0	8.455-4	8.4914+4	4.2744+3	6.433-4	1.7417+1	1.769+5
Minimum P_0 (1152.7)	1.1630+5	3.4070+1	1.054-4	9.0679+4	1.9387+3	7.774-5	4.8373+0	1.8005+5
Nozzle Lip (1649.9)	1.0895+5	4.6058+2	1.522-5	9.8549+4	3.0501+2	1.167-5	6.6007-1	1.8225+5

TABLE 12. (Concluded)

	HCN	H_2S	NH_3	NO	NO_2	SO	SO_2	SO_3
Chamber	5.7092+1	2.4023+1	5.7524+0	1.7398+3	6.812-1	2.0002+2	5.6035+2	1.6052-1
Throat	3.0790+1	2.4814+1	3.7071+0	9.8273+2	2.388-1	1.8079+2	5.8990+2	1.1407-1
1-D Exit Plane	1.0504-2	2.6441+2	5.2735-1	1.3875+0	2.771-6	5.4139+1	4.7992+2	1.7469-3
Last Left Running Characteristic								
Nozzle Axis (1514.8)	9.5776-2	3.0163+1	1.6183+0	2.7963+2	2.399-3	1.4858+2	6.2947+2	5.1362-2
Minimum P_0 (1152.7)	2.4048-2	4.1801+1	6.0535-1	5.5358+1	1.239-3	1.1713+2	6.5652+2	1.7582-2
Nozzle Lip (1649.9)	1.1261-2	2.0442+2	5.1048-1	2.4319+0	6.886-6	6.4417+1	5.3320+2	2.5861-3

	CuCl
Chamber	5.5466+1
Throat	6.1270+1
1-D Exit Plane	1.9666+1
Last Left Running Characteristic	
Nozzle Axis (1514.8)	7.0635+1
Minimum P_0 (1152.7)	7.7479+1
Nozzle Lip (1649.9)	2.6695+1

TABLE 13. AFTERBURNING ANALYSIS (REACTIONS BEING CONSIDERED)

1.	$HCl + OH = H_2O + Cl$	20.	$H + HO_2 = OH + OH$
2.	$H + HCl = Cl + H_2$	21.	$H + O_2 + M = HO_2 + M$
3.	$OH + Cl = HCl + O$	22.	$O + H_2 = OH + H$
4.	$Cl + HO_2 = HCl + O_2$	23.	$O + HO_2 = OH + O_2$
5.	$ClO + OH = HO_2 + Cl$	24.	$OH + HO_2 = O_2 + H_2O$
6.	$H + Cl_2 = HCl + Cl$	25.	$H_2 + HO_2 = H_2O + OH$
7.	$O + HCl = Cl + OH$	26.	$H + OH + M = H_2O + M$
8.	$Cl + O_3 = ClO + O_2$	27.	$H + HO_2 = H_2 + O_2$
9.	$Cl + Cl + M = Cl_2 + M$	28.	$OH + H_2 = H_2O + H$
10.	$O + Cl + M = ClO + M$	29.	$N + O_2 = NO + O$
11.	$ClO + H = HCl + O$	30.	$NO + O + M = NO_2 + M$
12.	$O + ClO = Cl + O_2$	31.	$NO + ClO = Cl + NO_2$
13.	$H + Cl + M = HCl + M$	32.	$NO + O_3 = NO_2 + O_2$
14.	$O_3 + O = O_2 + O_2$	33.	$NO_2 + H = NO + OH$
15.	$O + O + M = O_2 + M$	34.	$N + NO = N_2 + O$
16.	$O + H + M = OH + M$	35.	$CO + OH = CO_2 + H$
17.	$H + H + M = H_2 + M$	36.	$CO + O + M = CO_2 + M$
18.	$OH + OH = H_2O + O$	37.	$CO + HO_2 = CO_2 + OH$
19.	$H + O_2 = OH + O$	38.	$NO + ClO = Cl + NO_2$

Note: The term M represents any third body in the reaction.

TABLE 14. HARPOON BOOSTER EXHAUST EFFLUENT CONCENTRATIONS

Species Concentrations (ppm)

X = 120 ft downstream of nozzle exit

P_c = 1800 psia

0.1 sec after first missile motion

V_{C_L} = 412 K T_{edge} = 408 K

V_{C_L} = 170 ft/sec V_{edge} = 134 ft/sec

Species	Concentration		Maximum Error (Percent)
	Centerline	Edge	
HCl	2932	2824	1
H_2O	8290	7985	1
CO	33	32	1
CO_2	3519	3390	1
Cl	193	186	5
Al_2O_3(S)	3.72×10^6 μg/m³	3.61×10^6 μg/m³	1
O_2	205 030	205 210[a]	1
N_2	779 480	779 870[a]	1
Cl_2	0.011	0.011	3
NO	0.04	0.04	1
SO_3	1.8	1.8	1
Cr_2O_3(S)	1.3×10^4 μg/m³	1.3×10^4 μg/m³	-
CuCl(L)	8.4×10^4 μg/m³	8.4×10^4 μg/m³	1.8

a. High concentration is from entrained air.

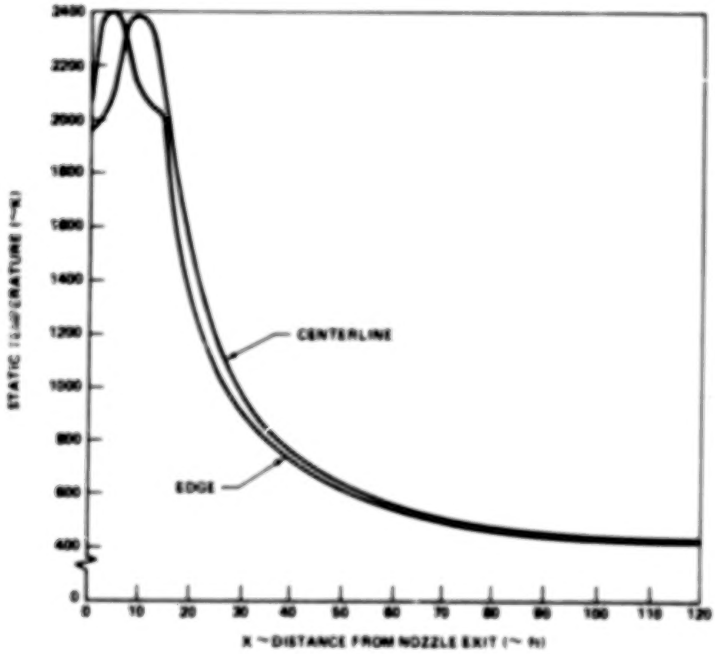

Figure 13. HARPOON booster afterburning analysis static temperature versus distance.

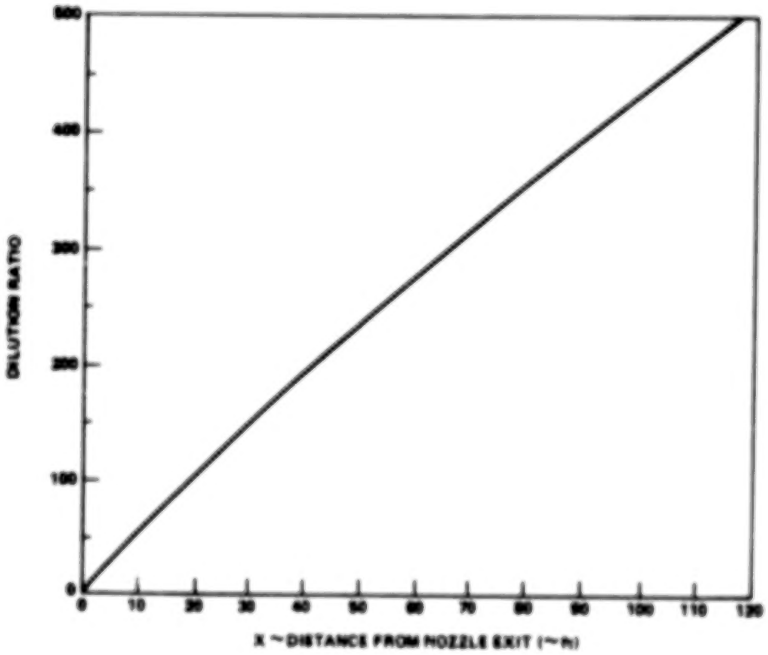

Figure 14. HARPOON booster afterburning analysis dilution ratio versus distance.

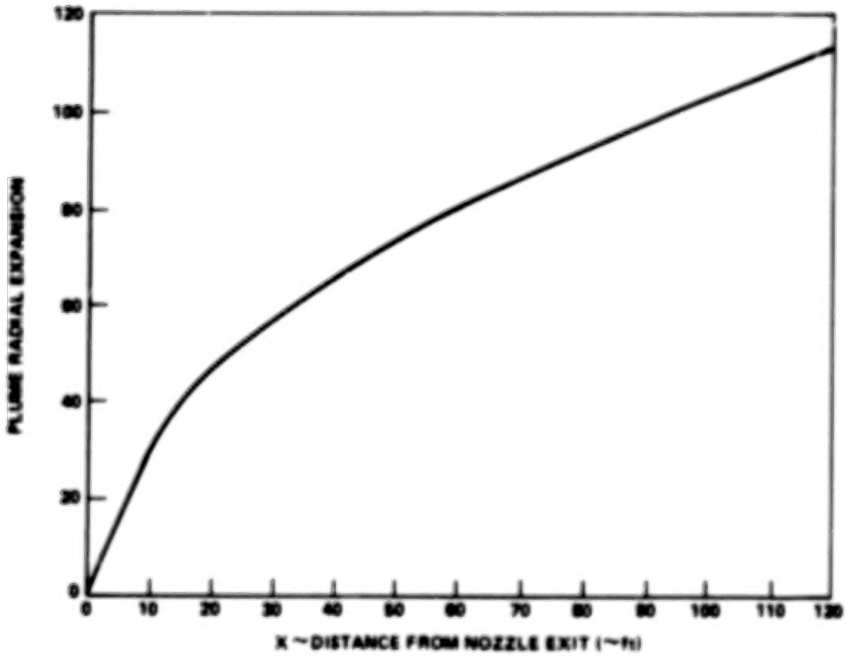

Figure 15. HARPOON booster afterburning analysis plume radial expansion versus distance.

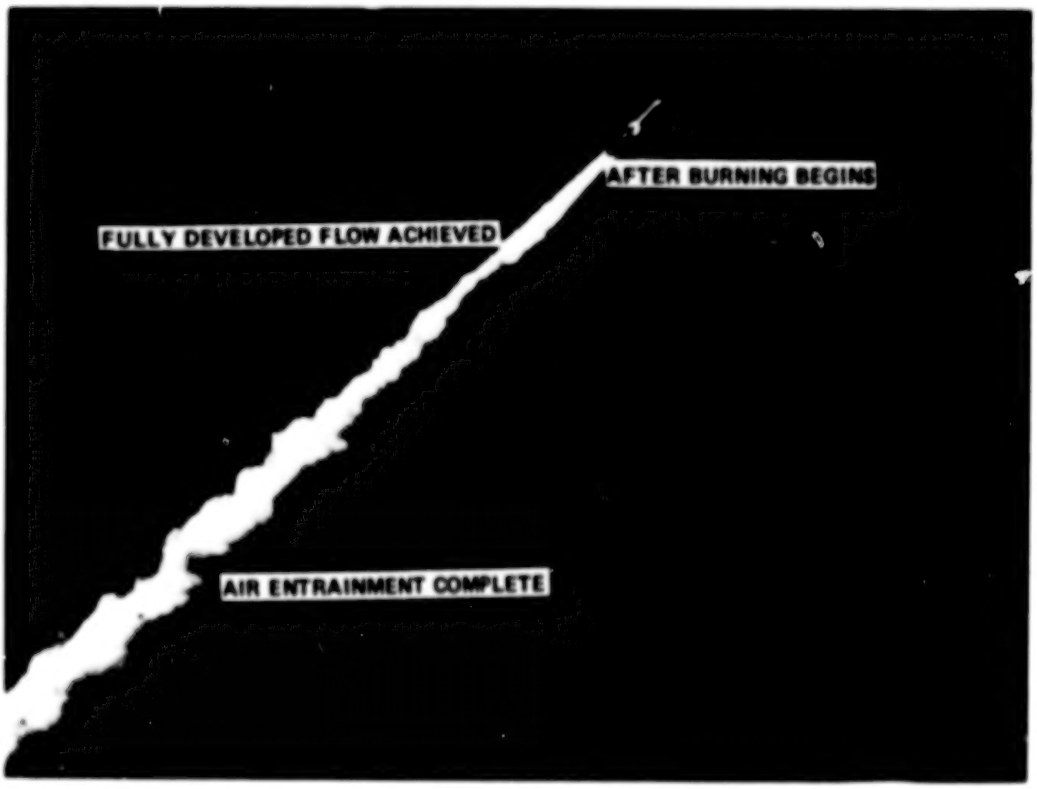

Figure 16. Photograph of HARPOON missile flight.

V. CONCLUSIONS

An analytical assessment of the exhaust effluents from the HARPOON booster was performed to identify the species present and determine their concentrations in the exhaust plume. An error analysis was conducted to determine the potential uncertainty in the assessment.

There were 95 candidate species (Table 3) considered in this investigation. From the two-dimensional, two-phase thermochemical nozzle analysis it was determined that the thermochemical environment would support the formation of only 28 species (Table 12) in significant concentrations (above 10^{-6} ppm) at the exit plane of the nozzle. Using the finite-rate thermochemical analysis to account for the flow from the nozzle as it mixes and reacts with the ambient air, it was determined that the thermochemical environment reduced the numbers of significant species to 13 (Table 14) at 120 ft downstream of the nozzle.

An error analysis of these results shows a maximum uncertainty in the concentrations of less than 1 percent in all but three cases. The uncertainty for Cl, Cl_2, and $CuCl_{(1)}$ was 5, 3, and 1.8 percent, respectively. Of these three species, the concentrations of Cl_2 and $CuCl_{(e)}$ are so far below toxic limits that they can be neglected. The maximum uncertainty in Cl is ±10 ppm; however, in terms of other potentially toxic species present in these exhaust effluents, this small uncertainty can be neglected.

This analysis clearly shows that the only species of potential concern are HCl and Al_2O_3 until the exhaust effluents become diffused into the atmosphere. Since monitoring Al_2O_3 would be complex and could not be done in real time, it is recommended that only the HCl be monitored. A recently developed analytical instrument, the Geomet, uses a chemiluminescent technique for the detection of HCl or total chloride ion and is used by the Environmental Protection Agency [17]. This instrument would be ideal for HCl detection. Thus, there is a minimum of analysis problems for the only gaseous species of concern.

The study has accomplished its two main purposes. First, it has predicted the exhaust species that are present and their concentration. Second, it has identified the species to be monitored. It has also found that there is no secondary species that can be used for monitoring purposes nor is there a need for one. The primary effluent of interest is easily, accurately, and inexpensively determined.

The analysis technique is general and can be used for any solid rocket motor. Each motor has a different chamber pressure history, nozzle configuration, and propellant formulation. The results presented in this report are valid only for the HARPOON booster motor; they cannot be used to draw conclusions for any other motor. If the exhaust effluents are of concern to personnel for assessment, each current and future motor should have similar analyses performed on it. For future motors, it would be most cost effective if the analyses were performed at an earlier stage of development and were made a permanent part of the standard development plan for a motor.

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16. ABSTRACT

The exhaust products from the HARPOON booster motors have been analyzed using both thermodynamic analysis and finite-rate chemistry. The resulting constituents are presented together with a discussion of the techniques employed.

† This study was accomplished in response to a request from the Naval Surface Weapons Laboratory as given in Navy Work Order Number N60921-76-MP-RD083.

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